

First-principles calculation of the piezoelectric tensor \vec{d} of III-V nitrides

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We report direct first-principles density-functional calculations of the piezoelectric tensor \vec{d} relating polarization to applied stress for the binary compounds AlN, GaN, and InN. The values of \vec{d} are rather sensitive to the choice of the exchange-correlation functional, and results are presented for both the local-density and gradient approximations. A comparison with experiment and with values predicted indirectly from the elastic \vec{C} and piezoconstant \vec{e} tensors is also presented.

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The piezoelectric tensor \vec{d} of a polar material relates to linear order the induced polarization \mathbf{P} to the applied stress via

$$P_i = \sum_j d_{ij} \sigma_j. \quad (1)$$

It is an especially relevant quantity in the field of III-V nitride compounds, whose piezoelectric and polarization properties are prominent [1] and unusual [2]. As implied by its definition, \vec{d} is relevant to electroacoustic applications [3], and to the determination of polarization and electrostatic fields induced by applied stress or strain in devices or epitaxial nanostructures [4].

The piezoelectric tensor \vec{e} [1,5] connecting polarization and strain ϵ_i via

$$P_i = \sum_j e_{ij} \epsilon_j, \quad (2)$$

is related to the \vec{d} tensor of interest here by

$$e_{ij} = \sum_k d_{ik} C_{kj}, \quad (3)$$

where the C_{ij} are the elastic stiffness constants at constant electric field. It is thus possible to compute \vec{d} from the knowledge of elastic constants and e -piezoconstants (using e.g. the theoretical estimates of Refs. [5] and [6], see also below). On the other hand, experiments [7–12] directly access the d_{ij} measuring the strain ϵ_i caused by an applied field \mathbf{E} via the converse piezoelectric effect

$$\epsilon_i = \sum_j d_{ij} E_j. \quad (4)$$

The d_{ij} 's in Eqs. 1 and 4 are by definition identical [13], so that a direct comparison is possible, and especially interesting and useful. Here we compute directly the d_{ij} constants in the III-V binary nitrides as derivatives of the polarization with respect to stress, calculating the Berry-phase polarization of a primitive cell explicitly subject to a given external stress. This approach enables us to directly compare the calculated values with experiment,

and with indirect theoretical predictions using Eq. 3, and separately calculated \vec{C} and \vec{e} tensors.

The binary III-V nitrides AlN, GaN, and InN crystallize in the wurtzite structure, and they possess three independent components of the piezoelectric tensor, namely d_{33} , $d_{31}(=d_{32})$, and $d_{15}(=d_{24})$. To compute these constants we run a damped Parrinello-Rahman-like dynamics [14,15] for each of the compounds considered, with the constraint that the system be subject to a given non-zero stress. The external stress is applied to the zero-stress equilibrium structure, which is identical to that reported in Ref. [5]. As a compromise between the contrasting needs for sufficiently large stresses to obtain polarizations outside the numerical noise, and for sufficiently small stresses to avoid large deformations and non-linearity, we separately apply stress components $\sigma_1 = \sigma_2 = \pm 50$ Kbar in the basal plane, and $\sigma_3 = \pm 50$ Kbar along the singular axis, to determine d_{31} and d_{33} ; for d_{15} we apply a shear stress $\sigma_5 = \pm 50$ kBar. In the case of InN, these stresses and the ensuing deformations may lead to metallization because of the very small calculated DFT band gap. This must be avoided because macroscopic polarization cannot be defined or computed in metallic systems. We found that the maximum applied stress had to be reduced to 5 Kbar for InN (incidentally, this does not cause numerical noise problems in the polarization calculations because of the very strong piezoelectric response of InN). After the bulk structure has been optimized for a given stress, the macroscopic polarization is computed using the Berry phase technique [16]. The stress derivatives of the polarization, i.e. the d_{ij} 's, are computed numerically using a standard two-points formula.

As for the technical ingredients, we worked in the Density-Functional-theory pseudopotential plane-wave framework using the VASP code [15] for structure optimization and a custom-made code for the Berry phase polarization. Ultrasoft potentials [15] were used for all atoms involved, and d semicore states were included in the valence for Ga and In. The results reported here were obtained with a plane-wave cutoff of 325 eV, and an (888) Monkhorst-Pack mesh [17] for Brillouin-zone

integration; these parameters were found sufficient to converge the computed stress for the systems considered. As the exchange-correlation functional, we used both the Ceperley-Alder [18] Local Density Approximation (LDA) in the Perdew-Zunger [19] parameterization, and the Generalized Gradient Approximation (GGA) in the variant of Perdew and Wang, known as PW91 [20].

In Table I we report all the d_{ij} 's calculated within GGA and LDA (the latter are given in square brackets), compared with indirect predictions obtained via Eq.3 using elastic and e -piezoconstants calculated separately [5], and with the available experimental data [7–12]. The calculated results depend considerably on the choice of the exchange-correlation functional, the LDA values being always larger than those of GGA. One can calculate the d_{ij} 's using elastic and e -piezoconstant data from e.g. Ref [5] and Eq. 3 to check consistency. These indirect prediction are reported for a subset of the d_{ij} in Table I with the label “indirect”, along with the percent deviations from the directly calculated values. The newly calculated C_{11} elastic constants, needed in the evaluation of the “indirect” constants, are also listed. The “indirect” values are always smaller than the directly calculated ones, and in most cases they are within $\sim 10\%$ of the latter. This suggests that the range of stresses considered here is in the linear regime, and proves the (approximate) consistency of the data with Eq. 3.

The available experimental values are as frequently above as below or within the GGA-LDA range; the deviation are in the range of $\pm 4\text{--}30\%$. From the comparison, it cannot be decided whether the LDA or GGA description is the most reliable. An exception is the shear constant d_{15} , which is described appreciably better by the LDA for GaN, a similar difference occurring also for InN, for which no experiment is available. This difference is presumably attributable to an incipient failure of GGA in describing accurately the shear elastic response of GaN and InN. There are no GGA calculations available for the latter; in turn, the LDA values of the shear constants by Wright [6] is in reasonable agreement with experiments.

Concerning the level of agreement of predicted and measured values, several points should be noted. *First*, all experiments were performed on constrained epitaxial samples. The epitaxial constraint affects the elastic and piezo response of the epilayer, and as a consequence two types of constants are generally reported [7], clamped (the one actually measured) and free-standing. The latter (with which we compare our calculations), are obtained from the former via a combination of compliance constants (the components of the inverse of \vec{C}). This adds some uncertainty to the comparison, given the large spread of the elastic constants values available. The maximum spread for GaN, for example, is as large as 1 pm/V [9] using different sets of elastic compliance constants.

Second, if the substrate on which the piezoelectric sam-

ple is grown is itself piezoelectric, the total deformation measured at the surface of the sample is likely to be influenced by the distortion of the substrate. For example, the two GaN samples used in Ref. [7] are respectively single-crystal (0001)-oriented GaN grown on SiC (0001), a piezoelectric material, and polycrystalline (0002)-oriented GaN grown on Si (100); the measured clamped constants are 2.8 and 2.0 pm/V in the two cases, which translates in free-standing bulk constants of about 3.7 (see Table I) and 2.6 pm/V respectively. Assuming the quality of the samples is comparable, and since polycrystallinity in wurtzites is mostly c -axial (vertical domains), a polarizable substrate may be argued to lead to a $\sim 35\%$ apparent increase in piezoelectric response. The lesser material quality of the polycrystalline sample may be invoked to dispense with it altogether; nevertheless, the argument serves to illustrate the point that the typical error bar expected in these experiments may easily increase to a few ten percent. Similar considerations may apply also to the measurements of Ref. [9] where a GaN/AlN/Si structure was used.

Third, a clear result of our calculations is that the ratio $R = -d_{33}/2d_{31}$ is never equal to 2 (it is in fact usually larger). This is to be attributed to the structural and response non-ideality of wurtzite nitrides. In Ref. [7], d_{13} was obtained from d_{33} assuming that $R=2$. Our results seems to invalidate this procedure, hence the measured [7] values of d_{13} .

In summary, we have obtained the piezoelectric tensor \vec{d} of III-V binary nitrides from first-principles LDA and GGA density-functional force-stress and polarization calculations. The results are consistent with previously calculated e -piezoelectric and elastic tensors. Agreement with experiment is only moderately satisfactory (deviations range typically between 4 and 30%). This may be attributed to experimental uncertainties such as the translation from clamped to free-standing measured values, and the response of polarizable substrates, as well as to theoretical uncertainties in the elastic response within GGA vs LDA.

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TABLE I. Stress-piezoelectric tensor \vec{d} in III-V binary nitrides, in pm/V. The values listed are: directly calculated within GGA and LDA (given in square brackets); calculated indirectly via separately calculated elastic and e -piezo tensors (labeled “indirect”; the deviations from the direct calculations are also listed); and experimental results (labeled “exp”). The experimental d_{31} constant was obtained [7] as $-d_{33}/2$ and is not listed here. The experimental value of d_{33} was obtained for a clamped sample, and the free-standing value reported here was inferred using the elastic response of the material. The C_{11} elastic constant needed in the evaluation of $\vec{d}^{\text{indirect}}$ are also listed, in GPa for both GGA and LDA (in square brackets).

Material	AlN	GaN	InN
d_{13}	-2.1 [-2.6]	-1.4 [-1.5]	-3.5 [-4.4]
d_{13}^{indirect}	-2.0, -5% [-2.4, -8%]	-1.2, -15% [-1.4, -3%]	-3.1, -12% [-3.8, -14%]
d_{33}	5.4 [6.4]	2.7 [2.7]	7.6 [8.4]
d_{33}^{indirect}	5.0, -8% [6.1, -5%]	2.4, -12% [2.6, -4%]	6.1, -20% [7.5, -12%]
$d_{33}^{\text{exp(a)}}$	5.6	3.7	
$d_{33}^{\text{exp(b)}}$	5.1	3.1	
$d_{33}^{\text{exp(c)}}$		2.6	
$d_{33}^{\text{exp(d)}}$	6.72		
$d_{33}^{\text{exp(e)}}$	5.53		
d_{15}	2.9 (3.4)	1.8 (3.3)	5.5 (8.5)
$d_{15}^{\text{exp(f)}}$	3.6	3.1	
C_{11}	506 [545]	414 [473]	266 [314]

- a) See Ref. [7]
b) See Ref. [9]
c) See Ref. [10], correction for clamping included.
d) See Ref. [11]
e) See Ref. [12]
f) See Ref. [8]